THE GENESIS OF BITUMENS, AS RELATED TO CHEMICAL GEOLOGY.

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1. On the 5th of February, 1897, a symposium was held at the rooms of the American Philosophical Society in Philadelphia, upon "The Origin and Nature of Petroleum." It was conducted by Profs. S. P. Sadtler and Charles F. Mabery, Dr. D. T. Day, of Washington, D. C., Francis C. Phillips and the writer. While listening to the papers then read, I was impressed with the fact that the discussion proceeded almost wholly without regard to any consideration of the different conditions that probably obtained in that primitive world in which the oldest petroleums found their origin. Prof. Mabery discussed, from the standpoint of pure chemistry, the composition of the petroleums of the Trenton limestone; I, myself, those of the Miocene Tertiary of California; Dr. Sadtler, the extremely interesting experiments that he had made upon the destructive distillation of the glycerides of linseed oil; while Dr. Day discoursed upon the somewhat remote and problematic resultant of certain chemical reactions upon bitumen; and Mr. Phillips presented some exceedingly interesting theoretical considerations concerning "The Genesis of Petroleum and Natural Gas" and "The Occurrence of Petroleum in the Cavities of Fossils." Later reflection has brought very forcibly to my mind considerations that I am led to present as a possible means of reconciling many of the differences that appear in the late discussion of these questions.[1]

2. In view of the general acceptance of the nebular hypothesis, it is unnecessary to establish the fundamental proposition that bitumens, as minerals, are properly considered in their relation to all the other mineral species that have been identified and described as together constituting the earth's crust. The clear distinction of these relations has followed upon many years of research along several lines. It began more than a century ago with the famous discussion waged between the Plutonists and Neptunists, as to whether fire or water had been most active in producing the phe-

[1] Proc. Amer. Phil. Soc., xxxvi, No. 154.

nomena of rock building. Mineral silicates were then supposed to have crystallized from igneous fusion, and the deposition of sediments to have resulted only in amorphous, uncrystallized rocks. The idea that heat and water together may have produced all of the phenomena that have been attributed to the action of either alone has been of slow growth; but may now be said to be pretty generally accepted, although there are those who refer to the action of heat and of pressure alone phenomena that are without doubt properly the resultant of the action of heat and steam under pressure.

3. The discussions that have proceeded along the three lines of geology, chemistry and mineralogy, have been mainly directed to an elucidation of the problems relating to the formation of the crystalline rocks. To determine, therefore, the nature of metamorphic action and the conditions under which it might take place, was the problem to the solution of which Bischof, Hunt, Delesse, Daubrée and several others of the most gifted chemical geologists of this century devoted themselves.[1] These gentlemen first considered the reactions that according to known chemical laws must follow the cooling of a heterogeneous mixture of the elements composing the earth, in a state of gaseous fluidity, and at a temperature that rendered chemical combination impossible; in other words, a state of complete dissociation. It follows that the most infusible elements would first condense and form a solid nucleus around which would float an ocean, in a state of igneous fusion, of more fusible elements and compounds, while over all would hover an atmosphere containing all the nitrogen and oxygen, the free hydrogen, sulphur and allied elements, with the chlorine and other halogens. As the cooling proceeded the silicon would combine with oxygen and bases, forming both acid and basic silicates, which would constitute a solid crust. The hydrogen and haloids combining would form the haloid acids and the sulphur and allied elements would form oxygen acids, all the hydrogen being oxidized into water, which with the acids would be alternately condensed and evaporated, falling as an acid rain upon the surface of silicated rocks, which in turn

[1] G. Bischof, *Chem. and Phys. Geology*, Cav. Soc. ed. T. S. Hunt, *Chem. and Geolog. Essays*. Delesse, "Essay on Pseudomorphs," *Ann. des Mines*, xii, 509; xiii, 393, 415; xvi, 317–392. *Mem. Acad. de Scien. de France*, xvii. Daubrée, *Comptes Rendus de l'Acad.*, November 16, 1857. *Études et experiences synthétique sur le Métamorphisme*, Paris, 1859.

would emerge from the ocean of water heavy with dissolved chlorides and sulphates, while an atmosphere dense with carbonic acid would help to maintain a temperature that would retard the cooling through vast cycles of geologic time, in the course of which, under conditions entirely different from any now known, vegetable and animal life would appear upon the earth, or, more properly, in the waters that covered the earth.

4. It is very evident that the chemical conditions obtaining in this remote geologic epoch, while not incompatible with the development of life, were, however, very different from those which have prevailed at any time since the advent of any of the higher forms of animals. We have a right to believe that at the dawn of life, of all the elements that enter into the composition of vegetable and animal tissue—carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur—nitrogen alone was wholly free. Carbon and hydrogen existed in combination with oxygen as carbonic acid and water. Phosphorus and sulphur were oxidized, and in combination with basic elements as salts. The excessive proportion of carbonic acid and aqueous vapor in the atmosphere gave to it the property of transcalesence, by which, while readily penetrated by heat from the sun, it refused to transmit this heat when reflected from objects at the earth's surface. This gave to the atmosphere properties similar to those of a greenhouse, by which so high a temperature was maintained during the coal period that semitropical plants flourished at the poles. At an earlier period, before terrestrial vegetation had removed the carbonic acid from the air, and before the surface of the cooling earth had lost its heat by radiation, the palæozoic (dawn of life) ocean and the land gave support to both vegetable and animal life, at a temperature that at the present time would destroy most organic forms.[1]

5. The strata which form that portion of the earth's crust which has been referred to the palæozoic era, are of enormous thickness and are found in different parts of the world, to present aspects strikingly similar. Messrs. Hall, Billings and Dawson, in North America, Salter and Hicks in England, Angelin in Sweden, and Barrande in Bohemia, have shown that the forms of animal life in that early period were very closely related, if not identical, in these widely separated areas; yet, below these formations, which hold the

[1] W. H. Brewer, *Am. Jour. Sci.* (2), xli, 389.

remains of marine animals, in Bohemia and Sweden if not elsewhere, there is a "region of fucoids," of great thickness, carrying back the dawn of vegetable life to a still more remote epoch.[1] Throughout the last fifty years, successive discoveries of fossils in strata hitherto supposed to be destitute of organic remains, have carried the apparent dawn of life back through successive geological formations, until the azoic (devoid of life) rocks have ceased to be appropriately named, and Mr. Hicks, speaking of the Cambrian fauna of Wales, says, "Though animal life was restricted to these few types, yet at this early period the representatives of the different orders do not show a very diminutive form, or a markedly imperfect state; nor is there an increased number of blind species. The earliest known brachiopods are apparently as perfect as those which succeed them; and the trilobites are of the largest and best developed types. The fact also that trilobites had attained a maximum size at this period, and that forms were present representative of almost every stage of development, ... blind genera along with those having the largest eyes, leads to the conclusion that for these several stages to have taken place numerous previous faunas must have had an existence, and, moreover, that even at this time in the history of our globe an enormous period had elapsed since life first dawned upon it."[2]

6. The formations that contain these earliest palæozoic forms of life are now found for the most part in a crystalline condition; yet, Dr. Hunt affirms, "that the oldest known rocks are stratified deposits of limestone, clay and sands, generally, in a highly altered condition; . . . . it is, however, quite certain that the advent of life in these oldest fossiliferous strata was subsequent to the period of chemical reactions on a cosmic scale."[3] The manner in which these geological formations and parts of formations may have been rendered crystalline has been very exhaustively discussed by Dr. Hunt in his chemical and geological essays. He has shown

[1] James Hall, *Paleontology of New York*, Vol. iii, Introduction. Billings, *Am. Jour. Sci.* (2), xxxii, 232. *Reports Geological Survey of Canada*, v. d. Dawson, *Canadian Naturalist*, v. d. *Reports Geological Survey of Canada*, v. d. Salter and Hicks, *Proc. Geol. Assoc.*, *Quar. Jour. Geolog. Soc.*, v. d. Angelin, *Palæontologica Scandinavica*. Barrande, *Bul. Soc. Geol. de France* (2), xvi, 529–545.

[2] Hicks, *Quar. Jour. Geol. Soc.*, May, 1872.

[3] *Chemical and Geological Essays*, ed. 1875, p. 2.

how fully his conclusions, based almost wholly on theoretical considerations, have been confirmed by the experiments of Daubrée, who was led to investigate this subject, from observing that the action of the alkaline, thermal waters of the spring at Plombières, at a temperature of 60°–70° C., had in the course of centuries given rise to the formation of zeölites and other silicated minerals among the bricks and cement of the old Roman baths.[1] He further shows that at a temperature of 100° C. silicates are produced from a reaction between alkaline silicates and carbonates of lime, magnesia and iron. He says further, "Now the supposed mode of formation of the primitive molten crust of the earth would naturally exclude all combined or intermingled water, while all the sedimentary rocks are necessarily pervaded by this liquid, and are consequently in a condition to be rendered semifluid by the application of heat. . . . . If now, we admit that all igneous rocks, ancient plutonic masses as well as molten lavas, have their origin in the liquefaction of sedimentary strata we at once explain the diversities of their composition. . . . . The presence of fossil plants in the melting strata would generate carburetted hydrogen gases, whose reducing action would convert the sulphurous acid into suphuretted hydrogen; or the reducing agency of the carbonaceous matter might give rise to sulphuret of calcium, which would be, in its turn, decomposed by the carbonic acid or otherwise. . . . . The carburetted hydrogen and bitumen evolved from mud volcanoes, like those of the Crimea and Baku, and the carbonized remains in the *moya* of Quito, and in the volcanic matters of the island of Ascension, not less than the infusorial remains found by Ehrenberg in the ejected matters of most volcanoes, all go to show that fossiliferous sediments are very generally implicated in volcanic phenomena."[2] Again, he states, that in a letter to Sir Charles Lyell, dated February 20, 1836, Sir John F. W. Herschel maintains that with the accumulation of sediments the isothermal lines of the earth's crust must rise, so that strata buried deep enough will be crystallized and metamorphosed, and eventually be raised with their included water to the melting point." Again Dr. Hunt says, "We conceive that the earth's solid crust of anhydrous and primitive rock is everywhere deeply concealed beneath its own ruins, which

[1] *Études et expériences synthétique sur le métamorphisme*, par M. A. Daubrée, Paris, 1859, p. 98; *Ann. des Mines* (5), xiii, 227.

[2] *Essays*, p. 8.

form a great mass of sedimentary strata, permeated by water. As heat invades these sediments, it produces in them that change which constitutes normal metamorphism. These rocks at a sufficient depth are necessarily in a state of igneo-aqueous fusion, and in the event of fracture of the overlying strata may rise among them taking the form of eruptive rocks."[1] He calls the effects produced by such invasion of eruptive masses, local metamorphism. From these extracts from several of Dr. Hunt's essays, it can be easily understood that a struggle has been in progress from the time of the oldest known rocks to the present, between the shrinking and wrinkling crust of a cooling earth and the thickening deposits of sediment accumulating from its erosion.

7. One Sunday in the early summer of 1866, I found myself with Dr. George L. Goodale, now of Harvard University, stranded at a small hostelry, at the San Fernando Pass, near the old Mission of San Fernando, in southern California. The day was very fine and we chose a morning climb to anything the hostelry had to offer; so, mounting our horses, we rode to the eastward over the flood plain of pulverized rock that at some former period had poured out of the great cañon back of where the town of Burbank now stands. We climbed one of the spurs of the San Rafael range to the west of the cañon. We first passed over rounded hillocks of sandy soil which as we ascended became gradually merged into soft fossiliferous sandstone. After a time the effects of heat became manifest. The clam shells and fossil clams, of which there were cart-loads, appeared crystalline, and the iron in the sand was no longer green but red. The sandstones became more dense and the clays were silicated. At length the strata passed into a micaceous gneiss and finally we found the central core of the mountain to be a light-colored fine-grained granite. About half way up, Dr. Goodale found a vertebra of a whale half buried in the sandstone and still very perfect in form, while I found a fossil pine cone that had evidently received some rough usage on the ancient beach. This cone contained some seeds that showed it to be closely allied to the nut pine of New Mexico. The mountain consisted wholly of Tertiary sediments that had been metamorphosed precisely as Sir J. F. W. Herschel had suggested in his letter to Sir Charles Lyell.

[1] *Essays*, p. 9.

8. It is not alone through a study of the crystalline rocks that the chemistry of the primeval world is interpreted. By a comparison of the kind and amount of salts dissolved in the waters of the primeval ocean that are enclosed in palæozoic strata with the kind and amount of salts dissolved in the waters of the present ocean, Dr. Hunt has shown that from the earliest geologic time until the present, alkaline carbonates derived from the subaërial decomposition of feldspar have been carried into the ocean by streams, and the calcium and magnesium in the ocean have been successively precipitated as carbonates, producing limestones and dolomites, while common salt and calcium sulphate have accumulated in the present ocean, the former in large excess. There is abundant evidence that this palæozoic ocean was hotter than the existing one, as well as more saline, while it is equally evident that during long intervals its sediments carried down vast quantities of the remains of vegetable and animal life. He has further repeatedly shown in what manner these sediments were influenced by the organic matters that were enclosed in them. In his essay on "The Chemistry of Natural Waters," he has shown that argillaceous sediments deprive waters of the organic matter in solution by forming a compound containing an organic radical. He says, "There is reason to believe that alumina is under certain conditions dissolved by waters holding organic acids," and cites melite and pigotite as examples of the compounds formed. He further shows that organic matter in water reduces sulphates to sulphides, producing from soluble sulphates of lime and magnesia carbonates of the basis, with hydrogen sulphide, free sulphur, or a metallic sulphide; the hydrogen sulphide being converted by slow oxidation or combustion, followed by absorption of oxygen directly into sulphuric acid, which is again, when in contact with organic matter, reduced to hydrogen sulphide.

He says with reference to the water of palæozoic brine springs, "In the large amount of magnesium chloride which they contain, these waters resemble the bittern or mother-liquor which remains after the greater part of the sodium chloride has been removed from sea-water by evaporation. . . . . The complete absence of sulphates from many of the waters points to the separation of large quantities of earthy sulphates in the Cambrian strata from which these saline springs issue; and the presence in many of the dolomite beds of the Calciferous sand rock of small masses of gypsum, abundantly disseminated, is an evidence of the elimination of sulphates by evaporation. . . . . The brines of the valley of the Allegheny river, obtained from borings in the coal formation, are remarkable for containing large proportions of chlorides of calcium and magnesium, though the sum of these, according to the examples given by Lenny, is never equal to more than about one-fourth of the chloride of sodium. The presence of the sulphates of barium and strontium in these brines, and the consequent absence of soluble sulphates, is, according to Lenny, a constant characteristic in this region over an area of 2000 square miles."[1]

Among many other illustrations that might be given of these non-sulphated palæozoic waters, I mention one which was obtained from a boring on Great Manitoulin island in Lake Huron, at a depth of 192 feet, "After passing through the black slates of the Utica formation, and for sixty feet into the underlying Trenton limestone. . . . . It contained no sulphates nor barium nor strontium." Another palæozoic water of a very different character was obtained from a well bored for petroleum at Bothwell, Ontario, in 1865. "At a depth of 475 feet from the surface, and probably at or near the base of the Corniferous limestone, a copious spring was met with of very sulphurous water and a little petroleum." The water contained sulphate of calcium and sulphides of sodium and hydrogen. Waters apparently similar are pumped from several of the oil wells in the vicinity. "The sulphurous impregnation is doubtless to be ascribed to the reducing action of hydrocarbonaceous matter upon the sulphates which the waters contain."[2]

9. A brief examination of the superposition of the palæozoic and earlier formations of North America will show the Laurentian, embracing the oldest known rocks of the globe, outcropping from the coasts of Labrador to Lake Superior and over a large area in northern New York. Associated with this system is the Norian, which is characterized by a great development of opalescent feldspars. Above these are the Green Mountain series, an inferior part of the Lower Silurian, which corresponds wholly or in part to the Huronian system of Canada and the region about Lake Superior. Above them are the White Mountain series, which are Upper Silurian and perhaps Devonian. These formations constitute for the most

[1] Bischof, *Chem. and Phys. Geol.*, i, 337. Hunt, *Chem. and Geol. Essays*, p. 121, ed. 1875. *Am. Jour. Sci.*, March, July and Sept., 1865.

[2] *Essays*, 158–163, ed. 1875.

part the rocks of Canada, New England, eastern New York and the eastern slope of the Alleghenies southward through New Jersey, Pennsylvania and Virginia. Speaking of these rocks, Dr. Hunt says, "In the oldest known of them, the Laurentian system, great limestone formations are interstratified with gneisses, quartzites and even with conglomerates. All analogy, moreover, leads us to conclude that, even at this early period, life existed at the surface of the planet. Great accumulations of iron oxide, beds of metallic sulphides and of graphite, exist in these oldest strata, and we know of no other agency than that of organic matter capable of generating these products.[1] . . . . Bischof had already arrived at the conclusion, which in the present state of our knowledge seems inevitable, 'that all the carbon yet known to occur in a free state can only be regarded as a product of the decomposition of carbonic acid, and as derived from the vegetable kingdom.' He further adds, 'living plants, decomposed carbonic acid, dead organic matters, decomposed sulphates, so that, like carbon, sulphur, appears to owe its existence in the free state to the organic kingdom.' As a decomposition (deoxidation) of sulphates is necessary to the production of metallic sulphides, the presence of the latter, not less than of free sulphur and free carbon, depends on organic bodies; the part which they play in reducing and rendering soluble the peroxide of iron, and in the production of iron ores, is, moreover, well known."[2]

Rocks of the Lower Cambrian in Great Britain as well as in North America are well known to exhibit carbonaceous remains. Of the former it is said, "They occasionally hold flakes of anthracite, and small portions of mineral pitch exude from them in some localities." The rocks of the Malvern hills contain fucoids. In the Quebec series on the south shore of the St. Lawrence, Hunt describes the occurrence of a carbonaceous substance, "entirely distinct from coal, which occurs in fissures, sometimes in the interstices of crystalline quartz. It is an insoluble hydrocarbonaceous body, brilliant, very fragile, giving a black powder, and results apparently from the alteration of a once liquid bitumen."[3] Similar material

[1] On the north shore of Lake Superior, I have found spherical concretions of graphite occuring in a rock that is apparently eruptive.

[2] *Essays*, pp. 301, 302. *Am. Jour. Sci.*, 1871.

[3] *Essays*, pp. 382, 396. W. Hodgson Ellis, "Analysis of Some Precarbōniferous Coals," *Chem. News*, lxxvi, 186, Oct. 15, 1897.

often lines cavities in the limestone in Herkimer county, New York, and not only sometimes encloses crystals of quartz, but is often enclosed in quartz crystals. These limestones are not crystalline.

Above these formations just mentioned, in the Carboniferous formation of both Europe and North America, anthracite occurs in metamorphosed strata. In Wales, Belgium, the Alps and France, such phenomena are frequent. The coal deposits of Massachusetts and Rhode Island are enclosed in highly metamorphosed strata. Much of the material is more nearly graphite than coal. Both the coal and the enclosing strata are so distorted that the bedding is destroyed and the material appears in segregated masses.

In the trap dykes that have penetrated the sedimentary formations of the Connecticut valley and New Jersey, veins of carbonaceous matter occur. These dykes are intruded masses, no doubt formed by the igneo-aqueous fusion of sediments that contained organic remains.[1]

10. With the exception of the exudation of mineral pitch mentioned above, I have seen no notice that bitumen occurs in crystalline rocks, but always in rocks adjacent to or above them. There are vast areas of the palæozoic formations of North America that are not crystalline, that have been more or less subjected to the action of steam and pressure at temperatures that have made them more or less the subjects of metamorphic action. Some of these rocks contain bitumen and others do not. The limestones in the bluffs of the Mississippi river at Minneapolis and St. Paul contain in the cavities of their fossils crystals of pyrite and rhomb spar. They immediately overlie the St. Peter sandstone and are said to belong to the Trenton group. Similar limestones in southern Michigan contain bitumen, free sulphur and sulphates in large amount. In southern Kentucky and Tennessee the limestones are often coarsely crystalline and contain large encrinite stems that are silicified. These same rocks contain geodes lined with crystals of quartz. Other geodes contain sulphates of barium, strontium and calcium, both with and without bitumen. In other localities the rocks of this age are filled with bitumen widely disseminated in small quantities. These rocks often exhibit very slight evidence of the effects of heat, but frequently are found immediately above or upon crystalline schists.[2]

[1] L. C. Beck, *Am. Jour. Sci.* (1), xlv, 335. I. C. Russell, *ibid.* (3), xvi, 112.

[2] S. F. Peckham, *Reports of the Tenth Census of the United States*, Vol. x, "Petroleum," p. 63.

11. In Prof. James Hall's celebrated Introduction to *The Palæontology of New York,* he shows that the earliest palæozoic sediments were deposited in a current that moved from southeast to northwest. Later the current moved diagonally across them from northeast to southwest. These later currents represent a vast interval of time, during which material accumulated to a depth of tens of thousands of feet of coarse sediments to the northeast in Canada, and growing finer diminished to the southwest in the Mississippi valley to a few thousands of feet. If metamorphic action is due to the accumulation of sediments, whereby the isothermal lines of the earth's crust rise to meet the increased pressure, by consequence of which sediments are brought into a state of igneo-aqueous fusion, it is not difficult to explain why, at a period in the earth's history, when the condition of the earth's crust, the ocean and the atmosphere, all contributed to maintain a high temperature, the strata as we pass from the southwest in the Mississippi valley towards the northeast should present, at the surface, increasingly the effects of heat.[1]

12. Let us now turn to Technology and see what the experience of more than half a century can teach us in relation to this question of the origin of Bitumen. Soon after 1830, Reichenbach in Germany,[2] Sèlligue in France and Gregory in Scotland, all worked upon the destructive distillation of pyroschists, wood, coal, peat and petroleum. They all discovered paraffine, and what is suggestive, they all propounded the idea that bitumens are distillates. They established the fact that pyroschists, wood, coal, etc., when destructively distilled yield paraffine and the oils found in petroleum. Sèlligue established quite a valuable industry in France, using as his raw material the schists of Autun. About 1850, the Scotch paraffine-oil industry arose. The raw material was a shale, called Boghead mineral, that was well known to contain fossil fishes. The distillate of this mineral closely resembled petroleum, and when petroleum was discovered in the United States in commercial quantities, the refineries on the Atlantic coast, that had been importing the Boghead mineral, commenced to work petroleum with slight changes in their processes. At the same time, the

[1] *Nat. Hist. of N. Y.*, "Palæontology," iii, 45–60.

[2] *Jour. für Chem. u. Phys.*, von Schweiger-Seidel, 1830, lix, 436. *Trans. Roy. Soc. of Edinb.*, xiii, 124. *Rep. of Pat. Inven.*, n. s., iv, 109. *Jour. des Connaisances Usuelle*, Dec., 1834, p. 285. Dingler, lvi, 40.

Albertite of New Brunswick was also being distilled on the Atlantic coast, while west of the Alleghenies cannel coal was being distilled at Cannelton, on the Kanawha river, in West Virginia; at Cloverport, on the Ohio river, in Kentucky; at Newark, O., and near Pittsburgh, Pa. The experiment of distilling oil from Devonian pyroschists was also made at Erie, Pa. They yielded fifty gallons of distillate to the ton. Without exception every one of these materials yielded paraffine, and when the petroleum obtained from Pennsylvania and West Virginia was used as a substitute, it was found that it yielded identical products, and the coal-oil industry was quickly rendered unprofitable. In an attempt to utilize all available material, William Atwood, who was one of the most skillful technologists in coal oil, was sent to the Island of Trinidad, where a plant was constructed and an unsuccessful attempt made to prepare illuminating and lubricating oils from Trinidad pitch. The pitch furnished distillates very different from the paraffine products obtained in the United States.

During the last years, before the coal-oil industry ceased to be profitable, a number of patents were granted for improvements in this technology, mainly for improved methods of distillation. The aim of these inventions was to effect a uniform heating of the material by which a slow distillation at low temperatures would be promoted. The presence of steam, often superheated, was found to be at all times beneficial. While to produce gas from these materials, it was found necessary to thrust them into a retort heated to a high temperature; to produce oil, it was found on the contrary best to distill at the lowest temperature possible. The intermediate oils, too dense for illumination and too light for lubrication, accumulated in the refineries, until Joshua Merrill discovered that by distilling them in such a manner that the vapors were superheated the vapors were "cracked" or "dissociated," and when they were condensed they were found to be of such a specific gravity that they could be used for illumination. This was the most important discovery ever made in the technology of bitumens, and when applied to the manufacture of paraffine petroleums it was of enormous value.

Soon after 1860, attempts were made to treat the bitumens of southern California by the same methods of distillation that were employed in treating paraffine oils, but all the results obtained showed that the processes were being applied to different materials and the results were different. These results all pointed to an excess of carbon and more unstable compounds. On analysis these crude oils were found to contain a large percentage of nitrogen as compared with paraffine petroleums.[1]

Canadian petroleum had been known to contain sulphur and to be difficult to refine. When similar oils were obtained in large quantities about 1885, in western Ohio, the sulphur petroleums became a serious problem in the technology of bitumen, as it was commercially desirable to treat them in the same manner as the pure paraffine petroleums of Pennsylvania. During 1893 and 1894, the technology of California bitumens was again investigated. Destructive distillation when applied to these bitumens, resulted in the production of a large volume of gas and asphaltic residuums with a distillate consisting principally of unsaturated hydrocarbons. The crude oils were found to be allied to the crude oils produced in the Scotch shale-oil industry, as they contain a large percentage of nitrogenous basic oils.[2]

There were thus established among North American bitumens three great classes: those known as "Pennsylvania oils," consisting of nearly pure paraffines, for which I have elsewhere proposed the name of Warrenite; those known as "Lima oil," which together with the Canadian oils contain a notable proportion of sulphur compounds, for which I have proposed the name of Maberyite, and the California oils, which occur in great variety and, while containing sulphur, are characterized as nitrogen bitumens and for which I have proposed the name of Venturäite. There is also a class of bitumens not yet investigated that are found on the eastern slope of the Rocky mountains from Mexico to the Arctic circle. In Europe, the paraffine petroleums of Galicia appear to be quite distinct from the bitumens of the Caspian sea. Technology has also divided bitumens into two great classes that are largely determined by geological occurrence. The great petroleum region of North America, which is by far the most important in the world, lies in the great palæozoic basin that surrounds the Cincinnati anticlinal; while the bitumens of California, the West Indies and Europe issue from Tertiary rocks. These Tertiary bitumens are found in much greater

[1] S. F. Peckham, *Reports Geol. Surv., California*, "Geology," ii, Appendix, p. 73.

[2] S. F. Peckham, *Am. Jour. Sci.* (3), xlviii, 250.

variety and are uniformly more difficult to refine into commercial articles than the bitumens obtained from older formations.[1]

It is proper to mention in this connection three classes of investigations that have been made on a commercial scale. The first was made about 1860–65, by Cyrus M. Warren, and consisted in distilling destructively the lime soap made from menhaden (fish) oil. The products of this distillation were refined into illuminating oil, in all respects identical with coal oil and refined petroleum; and they were also proved by an elaborate research to contain the same constituent hydrocarbons. Quite recently, Prof. Karl Engler, has repeated these experiments with the addition of pressure and steam during distillation. Warren's results were confirmed. Still more recently, Dr. S. P. Sadtler has discovered that the vapors escaping from linseed oil while being boiled furnish, when condensed, a petroleum-like liquid, which upon examination was found to consist of hydrocarbons identical with those found in Pennsylvania petroleum. It is an honor to American science that these results, valuable and interesting alike to science and technology, were obtained by American investigators.[2]

The general conclusion from technology appears to be, that for commercial purposes, crude bitumens and the products of their distillation may be duplicated by products of the destructive distillation of pyroschists, wood, coal, peat and a great variety of animal and vegetable substances.

13. It would be entirely unnecessary for my present purpose to notice in detail all the researches that have been undertaken upon bitumen, in all its various forms, since de Saussure published his paper on the *Naphtha of Amiano*, in 1817. It is sufficient to indicate along what lines the investigations have proceeded and in what manner the results have been interpreted. The earliest investiga-

[1] Boverton Redwood, *Petroleum*, etc., London, Charles Griffin & Co., 1896, ii. S. F. Peckham, PROC. AM. PHIL. SOC., x, 445. *Repts. 10th Census, U.S.*, x. "Petroleum," *Am. Jour. Sci.* (3), xlviii, 250 and 389, l, 33. *Science* xxiii, 74. *Jour Frank. Institute*, Nov., 1895. S. P. Sadtler, *Am. Jour. Pharm.*, Sept., 1896. C. F. Mabery, *Jour. Frank. Institute*, cxxxix, 401. *Proc. Am. Acad.*, n. s., xxiii. *Am. Chem. Jour.*, xix, 243, 374, 419, 796. B. Silliman, Jr., *Am. Jour. Sci.* (ii), (xliii,) 242. *Chem. News*, xvii, 257. *Bul. Soc. Chem. de Paris*, 1868, p. 77.

[2] C. M. Warren and F. H. Storer, *Mem. Am. Acad.*, n. s., ix, 177. Karl Engler, *Berichte der Deut. Chem. Geselschaft*, 1888, xxi, 1816, xxii, 592. Dingler, *Poly. Jour.*, 1889, p. 271. S. P. Sadtler, *Am. Jour. Phar.*, Sept., 1896.

tors analyzed bitumens as if they were homogeneous substances. They determined the carbon and hydrogen, added the percentages together and subtracted the sum from one hundred, calling the deficit oxygen. This went on for nearly fifty years. It is true that Prof. B. Silliman, Jr., fractionated petroleum by distillation, and queried whether the liquids that he obtained were educts or products. It was not until 1863 that Schorlemmer, in England, and Pèlouze and Cahours, in France, published researches that professedly separated the compounds that were mixed together in petroleum. They were soon followed by Warren and Storer in the United States, who, by a superior method of condensation, succeeded in separating the hydrocarbons in coal-tar naphtha, naphtha from Pennsylvania and Rangoon petroleum, naphtha from lime soap of menhaden oil and also the hydrocarbons from oil of cumin. These researches established the existence in these liquids of several series of hydrocarbons, the members of which were identical, whether obtained from natural or artificial substances, and were also in many cases recognized as identical with chemical compounds already well known.[1]

Since these results were published, a great amount of work has been done with varying success upon a great variety of petroleums, in which work progress has been observed along two lines, viz., first, better methods of separation, and second, better methods of ultimate analysis. It is only quite lately, however, that Prof. C. F. Mabery has succeeded, by distilling *in vacuo* with Warren's hot condenser, in so completely avoiding decomposition by cracking as to reach results that are final. While this is said without any wish to disparage the work of other investigators, it must be said with a proper regard for truth.[2] There is, however, a vast amount of chemical research on record, a very complete *résumé* of which can

[1] Theo. de Saussure, *Ann. Chim. et de Phys.* (2), iv, 314–320. *London Jour. of Sci.*, iii, 411. B. Silliman, Jr., *Am. Chemist*, ii, 18. *Moniteur Scientifique*, No. 366. *Am. Jour. of Gas Lighting*, xvi, 83. Wagner's *Ber.*, 1872, p. 848. C. Shorlemmer, *Chem. News*, 1863, viii, 157; xi, 255. *Am. Jour. Sci.* (2), xxxvi, 115. *Rep. de Chim. Appliqueé*, 1863, p. 174. *Jour. für Phar.*, xxi, 320. J. Pelouze and Aug. Cahours, *Comptes Rendus*, lvi, 505; lvii, 62. *Ann. de Chim. et de Phys.* (4), i, 5. *Am. Jour. Sci.* (2), xxxvi, 412. C. M. Warren and F. H. Storer, *Mem. Am. Acad.*, n. s., ix, 121–176. *Am. Jour. Sci.* (2), xxxix, xl and xli. *Chem. News*, xii, 85, 261, *et seq.*

[2] C. F. Mabery, *Proc. Amer. Acad.*, n. s., xxiv; *Amer. Chem. Jour.* xix, 243, 374, 419.

be found in the exhaustive work of Mr. Boverton Redwood, which has given results sufficiently accurate for my purpose. These results may be generalized as follows :

The Pennsylvania petroleums are the purest paraffine petroleums known. They contain small percentages of olefines and traces of benzoles. The same hydrocarbons have been found in other petroleums, in the distillates from cannel coal, pyroschists, peat, wood tar, fish-oil soap, fish oil under pressure and linseed oil, and also from grahamite, albertite, ozocerite and many other substances of mineral and organic origin.[1]

The Lima and Canadian petroleums contain the paraffine series, with a notable proportion of sulphur derivatives of the paraffines, formed by substitution ; and also traces of benzoles and nitrogenous basic oils.[2]

The Russian oils contain the benzole hydrides and naphthenes.[3]

The California oils, so far as at present known, consist of the benzole hydrides, naphthenes, benzoles and sulphur substitution compounds with a large percentage of esters of nitrogenous basic oils.[4]

The Scotch shale oils contain paraffines, olefines, benzoles and esters of nitrogenous basic oils.[5]

These esters are also found in coal tar and in Dippel's oil, the latter being an oil obtained as a distillate from the gelatine of bones.

No satisfactory research has ever been undertaken upon semi-fluid malthas or solid asphaltums. They cannot be distilled without decomposition, and no analysis by solution has yet been made that was not highly empirical. It is assumed, rather than proved, that many solid bitumens contain oxygen. They certainly do contain sulphur, and in some instances they contain nitrogen. When distilled upon the large scale solid bitumens are decomposed and

[1] Schorlemmer, Pelouze et Cabours, Warren and Storer, Mabery, *loc. cit.*

[2] Mabery and Smith, *Proc. Amer. Acad.*, n. s., xxiii ; *Amer. Chem. Jour.*, xvi, 83, 89, 544 ; xvii, 713 ; xix, 419.

[3] Beilstein and Kurbatow, *Ber. d. D. Chem. Ges.*, 1880, p. 1818. *Jour. Amer. Chem. Soc.*, xiii, 232. Markonikow and Oglobini, *Ber. d. D. Chem. Ges.*, xviii, 2234 ; *Ann. de Chim. et de Phys.* (6), ii, 372.

[4] S. F. Peckham, PROC. AMER. PHIL. SOC., x, 445 ; xxxvi, 154 ; *Amer. Jour. Sci.* (3) xlviii, 250. C. F. Mabery, *Jour. Frank. Inst.*, cxxxix, 401. Boverton Redwood, *Petroleum*, i, 203.

[5] English patents.

nothing but decomposition products are found in the distillate, while coke remains in the still. These decomposition products are very varied. Those that are geologically old yield paraffine, while those that are recent do not.[1]

Prof. Mabery has remarked that all petroleums contain the same proximate principles in different proportion. While this statement may be absolutely true, it is not so relatively. The palæozoic bitumens have been most carefully studied and they consist mainly of paraffines. The Tertiary bitumens have been less carefully studied, and they consist principally of benzoles and their derivatives in great variety. Mingled with these are the olefines and other series of hydrocarbons in small proportion, with an immense number of oxygen, sulphur and nitrogen derivatives and substitution compounds, the existence of which has been only recently suspected.

It can, therefore, be asserted that the natural bitumens and the substances resembling them that are obtained by the destructive distillation of mineral and organic substances, are strikingly similar. The palæozoic bitumens bear a resemblance to the simple distillates produced in the presence of steam, at low temperatures, when nitrogen is practically absent. The Tertiary bitumens resemble the distillates obtained at higher temperatures and when the raw material is rich in animal remains. There are, however, a large number of bitumens that have been too little investigated to admit of any generalizations concerning them. In illustration of this statement I would call attention to the valuable papers of Prof. Henry Wurtz, in which he shows that many so-called native paraffines are probably olefines.[2] I would suggest that some of them may be the higher naphtenes, that have the same percentage composition as olefines. The solution of these problems awaits a vast amount of research.

14. In the preceding pages I have given an outline of the views generally held by chemical and physical geologists concerning the chemical phenomena attending the cooling of the earth and its shrinking and contracting crust. To these I have added a *résumé* of the technical and chemical knowlege we possess concerning bitumens. I shall now proceed to discuss, in the light of these facts,

[1] S. F. Peckham and L. A. Linton, *Amer. Jour. Sci.* (4), i, 193. S. F. and H. E. Peckham, *Jour. Soc. Chem. Industry*, xvi, 424; H. Endemann, *ibid.* xv, 871; xvi, 121.

[2] H. Wurtz, *Eng. and Min. Jour.*, xlviii, 25, 114; li, 326, 376.

the occurrence of bitumens and the relation of such occurrence to their probable origin.

Leaving the problems of orography to the physical geologist for solution, there are a few suggestions to be made relating to these problems that I have not seen anywhere mentioned. If we regard the dizzy heights of the Andes and Himalayas, or the profound abysmal depths of the Pacific as isolated phenomena, they appear on a scale of oppressive grandeur and immensity; yet these irregularities in the earth's crust reach a maximum of only about ten miles in vertical height, which is only one twenty-five hundredth or four hundredths per cent. of the circumference of the earth at the equator. The local foldings of a few hundreds of feet in disturbed strata are microscopic when compared with the earth's diameter; and yet we are accustomed to regard these plications of strata as the result of sudden movements in the earth's crust. This is a pure assumption. The period of time through which critical observations of geological phenomena have been made when compared with the time that has elapsed since life dawned upon the earth is also microscopic; it is a smaller fraction than four hundredths per cent. The element of time in geological phenomena is only just beginning to be appreciated. We have learned from a few years of observation that some continental masses are rising and others falling with reference to the sea level; yet no one has observed these movements through many centuries, nor have these vertical movements of the coasts of the world been co-related and the laws that govern such movements been determined. We do not know whether a continent has emerged from an ocean maintaining a constant level, or whether the ocean has receded as the contracting mass has rendered the ocean depths more profound, or, as is more probable, the shrinking of the crust has changed the distance of the ocean surface from the centre of the earth, rendering the elevations apparently greater. It is not material to this question that we should know. Nor is it of importance to consider whether the continued operation of forces at present active through countless centuries, or the repeated interjection of cataclysms of world disaster, has brought the earth to its present condition. Volcanic eruptions, earthquakes and floods, separately and unitedly, change the face of nature within our own generation; it is reasonable to suppose that they have acted from the earliest period of the earth's history to the present time with constantly lessening violence. It is true that the local effects of such phenomena as the earthquakes at Lisbon and Java and the Red River fault appear cataclysmic; yet these effects are microscopic when compared with the dimensions of the earth, and may have been, nay, probably were the culmination of a series of movements that had been in progress for immense intervals of time. I therefore believe that in stating the causes of those changes that have taken place at the surface of the earth as we now know it, one of the most important considerations is the unlimited periods of time through which the pressure due to accumulation of sediments and the consequent development of heat has acted upon those sediments, which in many instances were filled with water charged with mineral matter in solution. From the combined action of pressure, heat and steam, through unlimited periods of time, the constituent elements of sediments have been brought into every possible state of combination, from obsidian and pumice, which have been completely fused, through lavas, granites, gneisses, etc., to sediments in which there has been no change at all. As Dr. Hunt has fully shown, the action of thermal waters, which have been largely instrumental in producing these changes, has been often extremely localized both laterally and vertically, and may be greatly varied by the constituents of the sediments themselves.

15. If, then, we accept the hypothesis that all of the rocks as we now know them are sediments, whatever may be their present condition, we are forced to the conclusion that life first appeared upon the planet at a date too remote to be determined even in geologic time, and that the remains of organic forms have practically been a constant constituent of sediments from that time to the present. As might be expected, we find organic remains in every possible condition, from crystallized graphite to unaltered cellulose. Vegetable and animal remains are found in every conceivable condition of replacement and alteration. We find pseudomorphism in the strictest sense as well as metamorphic action developed in every possible degree. Nor can we assert that any of the older strata are free from such action, for metamorphism is, as the word signifies, a change of form, and no limits can be assigned to such change in either time, place or degree that are not arbitrary. There can be no question that as sediments have accumulated slowly so these changes have progressed slowly.

Nevertheless, following upon long periods of quiet, there appear to have been periods of cataclysmic violence, as when the vast lava sheets that form the table mountain of the Sierra Nevada were poured out, not from a single peak, but from a whole range of peaks; when the whole of southern Colorado and northern New Mexico and Arizona were covered with lava sheets thousands of square miles in extent; or when the valleys of West Virginia were upheaved, the Oil Break formed and the mass of plastic grahamite forced into the fracture; or when the basic rocks that form the mounds of iron porphyry in Cumberland and Foster, R. I., were thrust up from the deeps; and the trap dykes along the whole eastern borders of the Alleghanies were poured into fractures of local extent. But these convulsions that have brought basic porphyrys, basalts, trap dykes and local metamorphism to the surface, have in the physical and chemical operations of nature produced anthracites and anthracitic residues and not bitumens. Bitumens are not the product of the violence of volcanic or cataclysmic action, but of the gentler action of normal metamorphism exerted through long periods, during which the volatile bitumen has been distilled from sediments containing organic matter, and at the lowest possible temperature, without regard to time, as the sediments were pressed down to an isothermal that admitted first of their distillation and then of the conversion of the carbon residues into graphite.

16. Dr. Hunt has left hundreds of pages in which he has shown that the crystalline and eruptive rocks, as we know them, are altered sediments. His argument is conclusive that the carbon that they contain is derived from organic forms. When discussing bitumens he shows, first, that the pyroschists do not, except in rare instances, contain bitumen, and are not in the proper sense of the word bituminous. Secondly, he shows that the pyroschists do not, "whether exposed at the surface or brought up by boring from depths of many hundred feet, present any evidence of having been submitted to the temperature required for the generation of volatile hydrocarbons." Thirdly, he shows that as the oil occurs in the limestone it could not have been distilled. He further shows that the Utica slate that is beneath the lower Devonian limestones is unaltered, and adds, "More than this, the Trenton limestone, which on Lake Huron and elsewhere has yielded considerable quantities of petroleum, has no pyroschists beneath it, but on Lake Huron rests on ancient crystalline rock with the intervention only of a sandstone devoid of organic or carbonaceous matter.[1]

[1] T. S. Hunt, *Essays*, p. 169, ed. 1875.

I have already shown (§ 6) that sediments become crystalline at very low temperatures and that the crytalline schists below the lowest stratified rocks contain abundant evidences of organic forms. Are we to suppose that there was no intermediate zone in which normal metamorphism died out and faded into unaltered sediments? We ought to expect to find the pyroschists in their normal condition. We ought to expect to find the coal altered or unaltered, according to its proximity to the heated area. We should not expect to find the carbonized remains of organic forms in rocks containing bitumen; for we cannot suppose that those beds that yielded the bitumen by distillation were suddenly plunged into a condition of igneo-aqueous fusion by which the organic constituents were instantly converted into anthracite and gas. As a general rule the process of conversion must have been as gradual as the progress of deposition. We cannot assume that in every instance the anthracite is the residue from a distillation of which the distillate was completely lost. Moreover, the example cited in § 7 is a complete demonstration, occurring as it does in a region rich in bitumen, that the change from sediments to crystalline schists is progressive and involves the organic as well as mineral constituents of the strata.

17. If a traveler should leave Boston, Mass., and travel in a generally southwest direction toward San Diego, in southern California, he would encounter along his route a series of object lessons that would lead to but one conclusion. Whatever the age of the crystalline rocks of New England may be, they are certainly for the most part older than the Carboniferous. The small basin around Mansfield, Mass., extending into Rhode Island, which contains the anthracites of that region, is surrounded by crystalline rocks, and, indeed, the anthracite beds themselves are, as already stated, altered to a substance nearer graphite than coal. The coal slates contain only impressions of coal plants, and fossils of any description are extremely rare in the vicinity. Intrusions of trap are frequent, and cones of highly basic porphyrys are thrust up through all of the crystalline sediments at several points. The change of form has been very complete in respect to every constituent of the sediments.

Westward around New Haven, Conn., the bedding of the sediments has not been so completely obliterated, but the change in the organic constituents has been quite as general. In the gneissoid traps of that region, thin veins occur of anthracitic material, which alone remains to represent the organic constituents of the altered sediments. Continuing our course southwestward the same changed condition is observed in the crystalline schists of Manhattan Island, and across the Hudson through northern New Jersey. Intrusions of trap, too, are frequent through all this region and the sole representative of the organic constituents of the sediments is anthracitic residues.

On the western slope of the Catskills, through eastern New York, the crystalline rocks which exist at varying depths below the surface are overlaid with sediments which are frequently imperfectly metamorphosed, and as one moves westward into central New York and northeastern Pennsylvania, while the coal beneath the surface is anthracite and the residues before mentioned that fill cavities in the limestone are anthracitic, still the surface rocks show less and less signs of alteration. As the summit of the Alleghanies is reached and passed, the coal beds fade by insensible stages from anthracite into unaltered splint and cannel coals. The beds of slate also become beds of pyroschists, and the formations generally assume the aspect of unaltered sediments. On the western slope of the Alleghanies the surface descends much less abruptly than it ascends on the eastern slope. The dip of the formations is much greater than that of the surface, consequently the outcropping edges of newer formations are repeatedly encountered, until in western Pennsylvania and New York metamorphism has ceased to be a problem in surface geology. These surface rocks are, however, geologically all below the coal, which in eastern Pennsylvania is metamorphosed into anthracite. There is no arbitrary line that separates the unaltered from the altered strata. The successive formations have thinned out, and in general they continue to become thinner as we go southwest; but there is no anthracite between the crest of the Alleghanies and the mountains of Arkansas. Throughout the Mississippi valley, as we pass to the west, these formations outcrop and overlie each other precisely like the shingles on a roof, with the pitch reversed.

In the Bradford oil field, in McKean county, Pa., the drill penetrates a bed of porous sandstone that lies enclosed in impervious unaltered strata. It contains a few shells and fish bones, but no other fossils. Like the surface rocks it lies sloping toward the southwest, the lower portion submerged in salt water, the middle portion filled with petroleum and the upper portion filled with gas; both originally under an enormous pressure. In Warren county, farther to the southwest, the drill reaches petroleum not in the McKean county sand, but in a different sand, higher in the series. Still farther southwest, in Venango county, the surface rocks are still higher in the series and the drill reaches petroleum in a pebble conglomerate that outcrops at the surface to the northeast. These pebble conglomerates, known as the "Venango Oil Sands," formed great riffles in the currents of the primeval ocean. They are several miles long and a few rods wide, level on the upper surface, and rounded on the under surface to a feather edge at the sides. One is above the other and they are covered, when they contain petroleum, with a solid, impervious shell of silica, that the drill penetrates with difficulty. The uppermost of these conglomerates consists of spherical pebbles of yellow quartz, about as large as cranberries; the lowest consists of lenticular pebbles of very white quartz. In both cases the pebbles are cemented together at their points of contact leaving large open spaces. These conglomerates are sometimes replaced by coarse, porous sandstones; neither of these contain fossils of any kind. Still farther southwest, on Slippery Rock creek in Mercer county, and at Smith's Ferry in Beaver county, another sandstone, that is barren where it occurs in Venango county, yields petroleum above the pebble conglomerate. If a line be followed farther to the left, across western Pennsylvania and into West Virginia, the outcrops of the formations would rise successively in the scale until the oil would be found in the Mahoning sandstone, which lies at the top of the Lower Productive Coal Measures. Since the development of the Lima oil fields the range of rocks holding the petroleum reaches in Ohio, Canada and Pennsylvania from the Lower Silurian, Trenton limestone, to the Lower Coal Measures. These rocks embrace nearly the entire palæozoic formations of North America. Very few wells have been sunk below the petroleum-bearing sandstone, for the obvious reason that it involved a useless expense. One of the deepest wells ever drilled in the oil region of western Pennsylvania was Jonathan Watson's deep well near Titusville. This well went down through all of the oil sands and the Devonian shales beneath them, to a depth of 3553 feet, when just as it was abandoned a hard rock was struck which was supposed to be the Corniferous limestone, which is the oil-bearing rock of Canada. The interval between the oil sands and the bottom of the well was filled with Devonian shales, that underlie the Bradford oil sand and are supposed to extend from Allegheny county, New York, to central Kentucky; and in fact to underlie the entire petroleum region that produces Warranite—the pure paraffine petroleums. When "dry" or unproductive holes are drilled outside the productive areas, they pass, at the horizon of the oil sands, through a different rock, which is compact and incapable of holding petroleum. These underlying Devonian shales outcrop at Erie, Pa., and furnish there the material that on distillation yielded fifty gallons of distillate to the ton. Where this formation outcrops it is filled with fucoids and has yielded small petroleum and gas wells. The men who drilled Jonathan Watson's deep well told me that, "the soap stone (Devonian shale) became harder as they went down, and was redder in color, in fact, had been burnt like brick." In a comparatively few localities, petroleum has been found saturating rocks that lie one above the other. The upper rock invariably yields the most dense oil. In 1881 I saw a well in West Virginia, from which the same walking beam pumped at every stroke oil of 27 degrees from a depth of 255 feet and oil of 45 degrees from a depth of 600 to 700 feet.

18. I have never seen a specimen of graphite reported to have come from any locality between the crest of the Alleghanies and the Ozark uplift. This is an uplift of the palæozoic formation west of the Mississippi river, extending from central Missouri to central Texas. It resembles that of the Alleghanies, but is on a smaller scale.[1] The eastern slope is more abrupt than the western. The formations of the central portions, in Arkansas and the Indian Territory, are highly crystalline, graphite and anthracite are of frequent occurrence and are found on the western slope. On this slope also, but farther west, in unaltered strata immediately above the crystalline formations, bitumen occurs in enormous quantity and great variety. Over a large area in the northeastern portion of the Indian Territory heavy petroleums are found only a short distance beneath the surface, and, as I am informed, below the coal. South of the Red river, in northern Texas, bitumens occur saturating horizontal beds of sand that are intercalated between strata of more or less solid limestone. North of the Red river, in the Indian Territory, every rock formation that is at all porous appears to be

[1] J. C. Branner, "Former Extension of the Appalachians across Mississippi, Louisiana and Texas," *Am. Jour. Sci.* (4) iv, 357.

filled with bitumen. As far as I have investigated it, the bitumen is uniform in kind and quality. It has saturated beds of sand, strata of sandstone and limestone, some of which are hard and crystalline, others magnesian and almost as soft as chalk, some of them without fossils and some almost all fossils, and all of them conformable with the Upper Silurian and Lower Carboniferous rocks that enclose them. In one locality a sort of bituminous breccia occurs, of immense extent, consisting of fragments of limestone and quartzite cemented together with bitumen. In another an immense horizontal bed of sand, completely saturated with bitumen, is overlaid with thirty or forty feet of conglomerate that has been more or less penetrated with it.

Almost all the beds north of the river are in very sharp folds, that bring the strata to the surface nearly vertical, in eroded anticlinals that extend across the country in parallel lines, often many miles in length. What is of especial interest in this connection is the occurrence in the vertical limestones and sandstones of imperfectly saturated strata. The bedding varies from the thickness of paper to a few inches. The rock mass was usually most easily penetrated along the lines of the thinnest beds. Fractures which cross all these beds, including both the thin and thick ones, show the bitumen completely filling the thin beds and only partially penetrating the seams and the mass of the thicker cryptocrystalline strata. Nothing could more beautifully and clearly demonstrate the fact that the bitumen was not indigenous to these rocks, but had penetrated them while previously and as at present in their nearly vertical position.

19. Continuing our journey across the continent, bitumen is frequently encountered in positions contiguous to normal or local metamorphism, until we descend into the great valley of California, west of the Sierra Nevadas. Here the development of bitumen has proceeded on a scale of vast magnitude. On the western slope of the Sierras the region around Roseville, in Placer county, and the vicinity of the city of Stockton, are well known to be rich in natural gas.[1] There are localities on these slopes that have also furnished limited supplies of petroleum, but, as before stated, the bitumen deposits of California are principally found in the Coast Ranges, including the ocean area lying between the Santa Barbara

[1] W. L. Watts, *The Gas and Petroleum Formations of the Central Valley of California*, 1894.

islands and the main land. The richest deposits have been found in Ventura county, on the border line that separates the Cretaceous from the Lower Miocene. None of the bitumen is found in crystalline rocks; yet the evidences of both normal and local metamorphism, in strata not far distant from the bitumen-bearing rocks, are abundant. The late Eli W. Blake once visited the Santa Barbara islands and afterwards described to me the cascades of lava that had descended from the volcanic cones in the centre of the islands over precipices into the sea. Bitumen has exuded for more than a century from the unaltered strata, whose upturned edges form the bed of the ocean, between these islands and the main land. The Tertiary formations that constitute the bluffs of the coast east and west of Santa Barbara contain deposits of bitumen of enormous extent and exhibit evidences of metamorphic action still in progress. Almost every large bluff from Point Conception to San Diego contains a solfatera, the action of which leaves the Miocene shales, originally rich in organic matter, devoid of a trace of carbon.

The best petroleum wells of Ventura county lie in the cañons of the Sulphur mountain, one of the foothills of the Coast Ranges. Other wells are similarly located with reference to these ranges.[1] None of them have penetrated crystalline rocks; yet the core of the Coast Ranges only a few miles east of the wells of the Pacific Coast Oil Co., as Dr. Goodale and myself found, is granite. Fragments of crystalline rocks are washed out of many of the large cañons that head in the main Coast Range back of the foothills in which the oil wells are drilled. Deep drilling is extremely difficult in this region on account of the fragile character of the rocks. It might be impossible to carry a well down through all the bituminous strata to the crystalline rocks, but the fact that they are altered Miocene sediments and exist at a comparatively short distance below the surface does not admit of any question. The evidences of metamorphism, through the agency of hot, silicated water, are found everywhere. The formations contain abundant remains of highly organized animals; and the bitumens which they contain consist of benzoles and naphthenes, without an "appreciable amount of paraffines, if any."[2] They also contain sulphur and nitrogen. They are evidently

[1] S. F. Peckham, *Mineral Resources of the United States*, "Petroleum in California," 1894.

[2] Letter of C. F. Mabery to S. F. P.

the products of the distillation of highly organized animal tissue, as an effect of the accumulation of sediments, and of metamorphic action upon unaltered sediments, through granite and gneiss to lava and pumice.

20. If we turn from North America to Europe-Asia, the testimony of the most eminent observers seems equally convincing. Daubrée was satisfied that the origin of the bitumen was found in metamorphism. Other French chemical geologists were equally well-grounded in this belief. As early as 1835, M. Rozet read a paper before the Société Geologique de France in which he discussed the occurrence of asphaltic limestone at Pyrimont. He says, "The bituminous matter is found equally in the calcareous rock and the molass that covers it. It is evident the action that introduced it into the two rocks is posterior to the deposition of the latter. The manner in which it is distributed in great masses, which throw their ramifications in all directions, joined in such a manner that the superior portions generally contain less bitumen than the remainder of the mass, indicate that the bitumen has been sublimed from the depths of the globe. . . . . It may be objected that such basaltic rocks do not appear in all the extent of the Jura. To that I reply that they are found in the neighborhood, in Burgundy and in the Vosges and further, that in the changes in the surface of the soil, whether occasioned by fractures or by the disengagement of vapors, the plutonic rocks do not necessarily appear at the surface. Perhaps in the deep valleys of the Jura the basalts are of very slight depth. . . . . In the Val de Travers, near Neufchatel, similar phenomena are observed."[1]

In 1846, Mr. S. W. Pratt associated the occurrence of bitumen at Bastennes with the eruption of ophite in the Pyrenees.[2] In 1854, M. Parran remarks concerning the occurrence of bitumen in the environs of Alais, "whatever be the origin of these substances, whether they be due to interior emanations from fissures of dislocation or to circumstances exterior and atmospheric, it is evident that there was during the Tertiary period an asphaltic epoch in relation to which it is convenient to recall the numerous eruptions of trachytes and basalts which characterize that period, and have probably acted by distillation upon masses of combustibles hidden in

[1] *Bull. Geol. Soc. de France* (1), vii, 138.

[2] *Quar. Jour. Geol. Soc.*, ii, 80.

the bosom of the earth."[1] The anthracites of the Alps offer convincing proof that large amounts of organic matter have been involved in the metamorphic action that has prevailed in that region. In like manner the relation of the bituminous deposits of Galicia and Roumania to the crystalline rocks of those countries show the part that metamorphism has played in their occurrence.

21. No theory that refers the origin of the bitumen to any physical or chemical action that has prevailed on a cosmic scale can satisfactorily explain the differences that exist in crude bitumens. Mr. Phillips has added the testimony of chemistry itself to show the improbability of a chemical origin for bitumens on a cosmic scale. Dr. Day has shown the reasonableness of an hypothesis which regards the bitumens of Pennsylvania as distillates, but his idea that the variation in the petroleums of that region is due to the effect of filtration is, in my judgment, hardly tenable. In Pennsylvania the darkest and heaviest oils are nearest the surface. The sulphur content of bitumen is too wide a subject to discuss here in detail; yet it may be said in general that sulphur enters bitumens by a secondary reaction between the bitumen and the sulphates dissolved in natural waters. The freedom of Pennsylvania petroleum from sulphur has already been shown to be due to the absence of sulphates in the natural waters of the region in which they occur. As has already been stated, Prof. Mabery has shown that the sulphur compounds found in Lima oil are sulpho-paraffines. This would naturally follow the reduction of sulphates by paraffines, the reaction being a double decomposition in which sulphur is substituted for hydrogen in the paraffine. Filtration would not be likely to remove such compounds from solution in the other constituents of the petroleum.

In his discussion of the "Occurrence of Petroleum in the Cavities of Fossils," Mr. Phillips has offered some ingenious but wholly unnecessary suggestions to account for the presence of a nearly solid bitumen in the cells of a coral reef uncovered in a quarry. Petroleum occurs in the rocks of the oil regions filling cavities of every description. Geodes, fossils, sandstones, pebble conglomerates, porous limestones, the Chicago dolomite, gravel, anything and everything that has a cavity or a pore, has been found saturated with it. Why? Simply because the enormous pressure under which the bitumen has accumulated in the crust of the earth has

[1] *Ann. des Mines* (5), iv, 334.

forced it there. When it has entered cavities like those in the coral reef described by Mr. Phillips, the diminished pressure and evaporation have resulted in the escape of the most volatile constituents. When the reservoir of the Bradford field was first penetrated, the pressure was estimated at 4000 pounds to the square inch. Whether or not this estimate was approximately correct, the pressure was sufficient to throw the well casing and piping out over the top of a derrick and land it in a meadow near by. A short time after the famous Karg well was struck near Findlay, O., I, myself, saw a pressure gauge register 450 pounds per square inch. Burning gas wells in western Pennsylvania sent streams of flame into the air eighty feet in height. Notwithstanding this accumulation of the facts of experience during many years, writers still ignore the tremendous significance of such phenomena, and speak of these deposits of bitumen as if they resembled a turn-over or an apple-dumpling laid away by nature. Gas cannot have been held under such tremendous pressure through cycles of geologic time in reservoirs of porous rocks, from which it has been filtering, as suggested by Mr. Phillips.

The complete inadequacy of all these arguments was never more fully set forth than in the language used by Mr. Phillips: "The movement of the oil through the rock displaced from the interstices in which it had originally collected would have been accelerated as the transition from solid organic tissues to liquid had been advanced." The decomposition of organic matter *in situ* could never have occurred under any conditions of accelerated pressure of even moderate amount. The rocks must have been consolidated and capable of resisting pressure before, action and reaction being equal, the pressure could accumulate. These facts are themselves the strongest reason for belief that the bitumens were never formed *in situ* in the porous rocks that contain them, but were gradually accumulated in those porous rocks that had been previously overlaid with impervious strata capable of resisting the enormous pressure until the reservoirs were penetrated by the drill. The fact that in the limestone some fossil cavities are filled while others are empty lies in the further fact, that the lines of shrinkage and other fractures penetrated some of the fossil cavities while others remained intact.

22. Upon this hypothesis, that bitumens are distillates, all of the variations observed in bitumens of different geological ages are

easily explained. The earliest forms of animal and vegetable life are admitted to have been nearly destitute of nitrogen; hence when these forms accumulated in sediments, which, borne down by deposits above them, invaded an isothermal that admitted of their distillation, they must have been distilled, in the presence of steam, at the lowest possible temperature; they must have been distilled under a gradually increasing pressure, the extent of which depended upon the porosity of the sediments above them, up to the surface. They must also have been distilled under a gradually increasing temperature which would have been largely controlled by the pressure. While the temperature and the pressure would have in every instance been the least possible, with steam always present, these physical conditions would on account of the varying porosity and consequent varying resistance of the overlying mass have produced very great effects in some instances and very slight effects in others. As a consequence, we have in natural bitumens, as in artificial distillates, materials varying in density from natural gas to solid asphaltum.

If these distillates proceeded from materials that would yield paraffine, these permanent and stable compounds, from marsh gas to solid paraffine, remained in the receptacles that nature had provided for them until they were released by the drill. If, however, the distillates proceeded from sediments of a different geological age, containing animal and vegetable remains more highly organized, that would yield different series of hydrocarbons, with compounds of nitrogen, then a very different bitumen would be stored in these receptacles. Secondary reactions would convert these primary distillates into a great variety of substances. The contents of the original reservoirs, borne down and invaded by heat, might become involved in a second distillation at an increased pressure and temperature. Fractures of these reservoirs from excessive pressure might lead their contents to the surface along lines of contact of strata or with water containing sulphates by which an originally pure hydrocarbon would be converted into a sulphur bitumen. A nitro hydrocarbon, reaching the surface under these conditions, might, by the combined action of evaporation and reaction with sulphates, pass through all the varying degrees of density from petroleum to maltha and become finally solid asphaltum, and this through the lapse of time and abundance of material on a scale of vast magnitude.

23. Such, then, is the "Testimony of the Rocks," along a line which spans the western continent. Nearly the whole of this line has been brought under my own personal observation. There is also reason for believing that a line might be followed in the eastern continent from the North sea to Java that would furnish equally convincing proof. To this testimony is added that of chemistry, technology, mineralogy, and the chemistry of the cooling earth. Each supports and corroborates the other. We have no need to search for coke until we know that coke was formed. We have no need to assume, that in the laboratory of Nature high temperatures and rapid action were necessary to produce results, for which infinite periods of time and the lowest possible temperature were fully adequate.

24. Since this paper was written I am in receipt of the annual address of the President of the Geological Society of America—Dr. Edward Orton—read at Montreal, December 28, 1897; from which exhales the exquisite aroma of fine literature, as from all the other productions of its accomplished author.[1] In this address I note two very important observations. He says, in speaking of Mendelejeff's chemical hypothesis, "It is hard, therefore, to see why, the whole world over, petroleum is entirely wanting in the Archean, and exclusively confined to the stratified rocks. There is not an oil field in the world in rocks of Archean time." I pass this by without comment to notice his observation upon the gas wells drilled in Oswego and Onondaga counties, N. Y., one of which penetrated a limestone that was found between the Pottsdam sandstone and granite, and furnished a gas pressure of 340 pounds; the other at a depth of 120 feet, in the Trenton limestone, gave the gas pressure of 1525 pounds. Dr. Orton well says, "A rock pressure of 1500 pounds to the square inch stands for, nay demands, a hermetic seal." Speaking of the Pottsdam sandstone and the dark limestone beneath it, he says, "The drillings brought from these horizons seem normal in every respect. Certainly there is no hint of any transformation by heat. 'The smell of fire has not passed on them.' There is no carbon residue. The bituminous products found in them cannot owe their origin to the usual form of destructive distillation." It is not likely, that the usual form of destructive distillation as illustrated in a gas retort has obtained anywhere in the operations of nature. I regard the penetration of granite

[1] *Bull. Geol. Soc. America*, ix, 93.

beneath bitumen-bearing rocks as a most conclusive and unexpected support to the validity of the views that I have herein set forth. I therefore, with this argument, for the present leave the subject.

NOTE.—I have quoted thus fully from Dr. T. Sterry Hunt for two reasons; with all his eccentricities, he was a man of untiring industry and a profound interpreter of the phenomena of nature in the light of experiment. Therefore, no writer of recent years has expressed views that are entitled to more respectful consideration. He is also more widely quoted by both American and European writers upon the subject of the origin of bitumens, especially as an exponent of the doctrine that bitumens are indigenous to the rocks in which they are found, than any other author.

HERPETOLOGICAL NOTES.

BY JOHN VAN DENBURGH.

(Read April 1, 1898.)

1. *Bufo boreas in Alaska.*—In the winter of 1896, Mr. A. W. Greeley, a student at Leland Stanford Junior University, gave me for examination two toads which he had "taken swimming in a large lake near Prince William's sound, Alaska, July 15, 1896." These are typical specimens of *Bufo boreas*, distinguishable at a glance from *Bufo halophilus*, and its northern form *B. h. columbiensis*. Unless my memory fails me, no toad has heretofore been recorded as Alaskan, and these specimens are, therefore, of great interest, since they greatly extend to the northward the known range of this family, genus and species upon the Pacific coast.[1] One of these specimens contains eggs which must have been nearly ready for laying.

2. *On the Time of Laying of the Western Gopher Snake in Central California.*—Early in the month of July, 1897, I received a fine, moderately large specimen of the Western Gopher Snake (*Pituophis catenifer*), which had been captured a few days before "in a marsh near Palo Alto," Santa Clara county, Cal. During the next few days this snake lay almost motionless in a small box in my office in the California Academy of Sciences. On the afternoon of

[1] Toads have been reported from Gt. Bear Lake.